

Claims

1. Combination of at least one building material and a bath fluid for a method for directly printing elements and models characterized in that

(A) the building material contains at least one low-viscosity monomeric or oligomeric compound having a viscosity $< 200 \text{ mPa} \cdot \text{s}$, which polymerises in contact with the bath fluid by the polymerisation of at least one component, and

the bath fluid consists of an aqueous solution containing an initiator, which initiates the polymerisation of at least one ingredient of the building material, or

(B) the building material contains at least one low-viscosity multifunctional compound having a viscosity $< 200 \text{ mPa} \cdot \text{s}$ as a crosslinking agent and

the bath fluid contains oligomeric or polymeric compounds forming a branched-chain or crosslinked polymer by reacting with the building material.

2. Combination according to claim 1, wherein the building material contains a cyanoacrylate represented by the general formula $\text{CH}_2=\text{C}(\text{CN})\text{COOR}$, a mixture of cyanoacrylates or a mixture of one or more cyanoacrylate(s) with additional anionically polymerisable compounds, wherein the residue R comprises linear or branched, monosubstituted, polysubstituted or unsubstituted, aliphatic, cycloaliphatic or olefinic groups having 1 to 10 carbon atoms, monosubstituted, polysubstituted or unsubstituted aromatic groups having 6 to 18 carbon atoms and saturated, unsaturated and aromatic, 3- to 7-membered heterocyclic groups having one or more heteroatom(s) independently selected from N, S, O and P, which may be substituted by one or more substituent(s) selected from halogen (F, Cl, Br, I), hydroxyl, oxo, cyano, C_{1-8} -alkoxy, amino, mono or di(C_{1-8})alkylamino, nitro, thiol and $-\text{S}(\text{O})_n(\text{C}_{1-8})\text{-alkyl}$ ($n=0, 1, 2$) and the bath fluid is a basic aqueous solution.

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3. Combination according to claim 2, wherein the building material and/or the bath fluid contains further additives.
4. Combination according to claim 2 or 3, wherein the cyanoacrylate is methyl
5 cyanoacrylate, ethyl cyanoacrylate, butyl cyanoacrylate or 2-methoxyethyl cyanoacrylate or a combination thereof.
5. Combination according to anyone of claims 2 to 4, wherein the additional
10 anionically polymerisable compounds are selected from the group comprising cyclic esters, cyclic anhydrides and epoxides.
6. Combination according to claim 5, wherein the cyclic ester is 3,6-dimethyl-
1,4-dioxane-2,5-dione, the cyclic anhydride is maleic anhydride and the ep-
oxide is glycidyl methacrylate or butanediol diglycidyl ether.
7. Combination according to anyone of claims 2 to 6, wherein the basic aque-
ous solution is selected from the group of aqueous alkaline or alkaline earth
metal hydroxide solutions or alkaline metal phosphate solutions, the group of
aqueous amine solutions or the group of basic buffer solutions.
8. Combination according to claim 7, wherein the basic aqueous solution is se-
lected from sodium hydroxide solutions (0.05 to 5%), sodium carbonate solu-
tions (5 to 10%), aqueous solutions of lysine, guanidinium salts or phenyl
glycine and phosphate buffer solutions.
9. Combination according to anyone of claims 2 to 8, wherein the building ma-
terial contains an acidic stabilizer or a stabilizer leading to an acidic com-
pound, when contacted with water.
10. Combination according to claim 9, wherein the stabilizer is selected from the
group comprising sulfonic acids, carboxylic acids, organic phosphonic acids,
sulfur dioxide and hydrogen chloride.

11. Combination according to claim 10, wherein the stabilizer is methane sulfonic acid, ethane sulfonic acid, toluene sulfonic acid, formic acid or vinyl phosphonic acid.
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12. Combination according to anyone of claims 2 to 11, wherein the additives in the building material are selected from the group comprising surface-active compounds such as the sodium salt of lauryl sulfonic acid, dodecyl dimethyl (3-sulfopropyl)ammonium hydroxide and perfluorinated aliphatic polyesters.
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13. Combination according to anyone of claims 2 to 12, wherein the additives in the bath are selected from the group comprising compounds for adjusting the viscosity and the polarity such as ethylene glycol, glycerine, poly(ethyleneglycol), poly(propyleneglycol), poly(ethylene glycol-co-propylene glycol), poly(hydroxyethyl acrylate), poly(ethylene imine), polysaccharides such as starch, sugar derivatives, polypeptides such a gelatine, compounds for adjusting the surface tension, the density, the ionic strength and the pH such as amino acids, salts such as sodium chloride, calcium chloride, surface-active substances such as the sodium salts of lauryl sulfonic acid, esters of the sodium salt of sulfosuccinic acid, acrylic acid and poly(acrylic acid).
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14. Combination according to anyone of claims 1 to 13, wherein the building material or the bath fluid contains additional substances to improve the mechanical properties of the polymers obtained.
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15. Combination according to anyone of claims 1 to 14, wherein the building material or the bath fluid contains biochemically active substances to influence the properties of the polymers obtained.
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16. Combination according to claim 14 or 15, wherein these substances also polymerize at least partially.

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17. Combination according to claim 16, wherein the substances polymerize anionically.

5 18. Combination according to anyone of claims 1 to 17, wherein coloured elements can be obtained by adding dyes or pigments to the building material and/or to the bath fluid.

10 19. Combination according to anyone of claims 1 to 18, wherein the density of the bath fluid amounts to about 0.95 to 1.15 times the density of the building material, so that self-supporting structures can be produced due to the buoyant force, which are not destroyed by lowering the element below the surface of the fluid.

15 20. Use of a combination according to anyone of claims 1 to 19 in a rapid prototyping method for the production of an element having the steps of:

(a) producing an element layer on a building support by selectively applying the building material by means of a drop-on-demand technique,

20 (b) filling recesses in the element layer by applying support fluid (bath fluid) having a density higher than that of the building material in such a way that the upper side of the element layer and the support fluid form an aligned surface,

25 (c) producing an element layer on the aligned surface of the preceding layer by selectively applying building material by means of a drop-on-demand technique, the building material being applied in the surface areas formed by support fluid in such a sequence that it is added laterally to the parts of the element layer already applied,

(d) producing further layers by repeating steps (b) and (c), each time, and

30 (e) separating the element from the support fluid.

21. Use of a combination according to anyone of claims 1 to 19 in a rapid prototyping method for the production of an element having the steps of:

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- 5 (a) producing one or more element layers, preferably 1 to 5 layers, on a building support by selectively applying building material by means of a drop-on-demand technique, the building support being positioned in a bath fluid in such a way that the surface of the building support is 10 to 700 μm above the surface of the bath fluid,
- (b) lowering the building support, until the top layer of the element is completely lowered below the bath surface,
- 10 (c) raising the building support, until the top layer of the element is 10 to 700 μm above the surface of the bath fluid, with recesses in the top layer of the element being filled with the bath fluid,
- (d) producing further element layers (preferably 1 to 5 layers) by selectively applying building material by means of a drop-on-demand technique, wherein the new element layer(s) can also exceed the area formed by the preceding layers and wherein the parts of the new layer(s) not applied on the preceding element layers are supported by the bath fluid,
- 15 (e) producing further layers by repeating the steps (b), (c), and (d), each time, and
- (f) separating the element from the bath fluid.

20 22. Use of a combination according to anyone of claims 1 to 19 in a rapid prototyping method for the production of an element having the steps of:

- (a) producing an element layer on a building support by selectively applying a building material by means of a drop-on-demand technique, the building support being positioned in a bath fluid in such a way that the surface of the building support is positioned one layer thickness below the surface of the bath fluid,
- 25 (b) lowering the building support by one layer thickness,
- (c) producing a further element layer by selectively applying building material by means of a drop-on-demand technique, wherein the new element layer(s) can also exceed the area formed by the preceding layers and wherein the parts of the new layer(s) not applied on the preceding element layers are supported by the bath fluid,
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- (d) producing further layers by repeating steps (b) and (c), each time, and
- (e) separating the element from the bath fluid.

23. Use according to anyone of claims 20 to 22, wherein elements having different mechanical properties are obtained by using different combinations of building material and bath fluid.

24. Use according to claim 20 to 22, wherein elements having different colours are obtained by using dyes or pigments in the building material and/or in the bath fluid.

25. Element obtainable by a method described in anyone of claims 20 to 24.

26. Element obtainable from a combination of building material and bath fluid according to anyone of claims 1 to 19.

27. Polymer having an improved hydrolysis stability, obtainable by reacting a cyanoacrylate represented by the general formula $\text{CH}_2=\text{C}(\text{CN})\text{COOR}$, a mixture of cyanoacrylates or a mixture of one or more cyanoacrylate(s) with further anionically polymerisable compounds, wherein the residue R comprises linear or branched, monosubstituted or polysubstituted or unsubstituted aliphatic, cycloaliphatic or olefinic groups having 1 to 10 carbon atoms, monosubstituted or polysubstituted or unsubstituted aromatic groups having 6 to 18 carbon atoms and saturated, unsaturated and aromatic 3- to 7-membered heterocyclic groups having one or more heteroatom(s), independently selected from N, S, O and P, which may be substituted by one or more substituent(s) selected from halogen (F, Cl, Br, I), hydroxyl, oxo, cyano, C_{1-8} -alkoxy, amino, mono or di(C_{1-8})alkylamino, nitro, thiol and $-\text{S}(\text{O})_n(\text{C}_{1-8})$ -alkyl ($n=0, 1, 2$), with at least one cyclic ester, cyclic anhydride and/or epoxide in the presence of an initiator for anionic polymerisation.

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28. Polymer according to claim 27, wherein the cyanoacrylate is selected from the group comprising methyl cyanoacrylate, ethyl cyanoacrylate, butyl cyanoacrylate and 2-methoxyethyl cyanoacrylate or a combination thereof.

5 29. Polymer according to claims 27 or 28, wherein the cyclic ester is 3,6-dimethyl-1,4-dioxane-2,5-dione, the cyclic anhydride is maleic anhydride and the epoxide is glycidyl methacrylate or butanediol diglycidyl ether.

10 30. Use of a combination of a building material and a bath fluid according to any one of claims 1 to 19 for the production of three-dimensional elements.

31. Use of a combination of a building material and a bath fluid according to any one of claims 1 to 19 for the production of elements for the application in the field of medicine.

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